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Analysis of Nonylphenols and Phthalates from Food Contact Packaging using GC/MS/MS

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Introduction

The production of antioxidants and surfactants used for the manufacturing of plastics and rubber utilize alkylphenol polyethoxylates which degrade into a group of alkylphenols called nonylphenols. In addition to the nonylphenols, phthalates can migrate from the plastic packaging to the material it is in contact with[1]. Nonylphenols are not full degraded from sewer treatment procedures which leads to accumulation in river and ground water that can be absorbed by plants and animals. The concentration and composition of the nonylphenols and phthalates depend on the individual production of the plastic or rubber. Many of the previous application notes and publications utilized the semi-nonpolar capillary GC column, but that does not separate the isomers of the phthalates and nonylphenols required for confident peak integrations. The MRM transitions are not unique for the isomers; which means chromatographic separation is needed. In this work, the GC column and separation were optimized to obtain the ultimate detection limit for these analytes using a high efficiency ion source and MRM.

Figure 1. Agilent 8890 and 7010C GC/TQ

Experimental

Several different column phases were tested to determine which provided the best separation of a technical mixture of nonylphenols, phthalates and teraphthalates. These columns were all 30m x 0.25 mm x 0.25 µm dimensions: HP-5msUI, DB-17ms, DB-35, and VF-Xms. These all have different amounts of phenyl in the backbone as well as some proprietary chemistries to help with unique separations.

The nonylphenol calibration standard, phthalate mix and the terephthaplate solutions were purchased from Accustandard (New Haven, CT). These were mixed together and injected on each column, using a similar oven program, to evaluate the separation and select the best column.

For the sample extracts, 100 mg of four different plastic food packaging materials (plastic wrap, plastic sandwich bag, to-go #5 polypropylene and to-go #6 polystyrene) were placed in a vial with a 10 mL of 4:1 hexane:ethyl acetate solution. The vials were sonicated at 60°C for 30 min. The extraction was dried under a low flow of N_2 to dryness. 1 mL of fresh solvent was added and the sample was decanted into a clean glass vial and centrifuged for 10min at 10,000 rpm.

Table 1. GC/TQ Acquisition Parameters

GC and MS Conditions:	GC/TQ (7010C)
GC	8890
Column	DB-35MS UI, 20 m, 0.18 mm, 0.18 µm
Inlet	MMI, 4-mm UI Fritted Low
Injection volume	1 µL
Injection mode	Cold Pulsed-Splitless; 40 psi for 1.1 min
Inlet temperature Air Cooled	50°C; hold 0.05 min
	600°C min^{-1} to 280°C
Oven temperature program	70°C for 1 min; 30°C/min to 200°C, 15°C/min to 235°C; hold 0.5 min, 5°C/min to 245°C, 45°C/min to 300°C; hold 2.73 min
Carrier gas	Helium
Column flow	0.9 mL/min
Transfer line temperature	300°C
Quadrupole temperature	150°C
Source temperature	280°C
Collision Cell Flows	4 mL min^{-1} He; 1.5 mL min^{-1} N_2
Acquisition Mode	dMRM

GC Optimization:

It does not matter how sensitive or unique the MS you are using is if the analytes cannot make it through the inlet and column. The UI low fritted liner was selected to help volatize the high boiling phthalates as well as the increased surface area allows for cold injections to minimize analyte degradation. Figure 2 illustrates the benefit of a cold injection with respect to a reduced shoulder and better response.

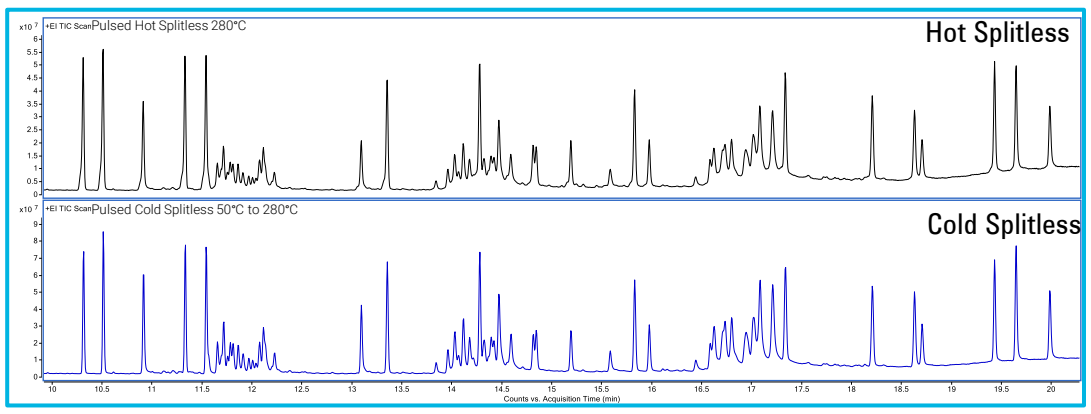

Figure 2. Comparison of the different inlet modes to reduce peak shoulders for the early eluters and increase signal intensity. The black chromatogram was created with an isothermal hot pulsed splitless injection while the blue was from a cold pulsed splitless injection that ramped to 280°C.

Optimal chromatographic separation was more difficult due to the additional phthalates and terephthalates added to the nonylphenol technical mixture. All of the analytes include a central phenyl group but the functional group lengths, compositions and positions dictated the retention on the different phases of columns. A small set of the phenyl backbone class columns were selected to identify the version the reduced co-elutions. In order of increasing polarity; HP-5ms, VF-Xms, DB-35ms, and the DB-17ms were all tested for this analysis. The phthalate and terephthalate pairs were the first set of analytes that were reviewed to determine the best phase (Figure 3).

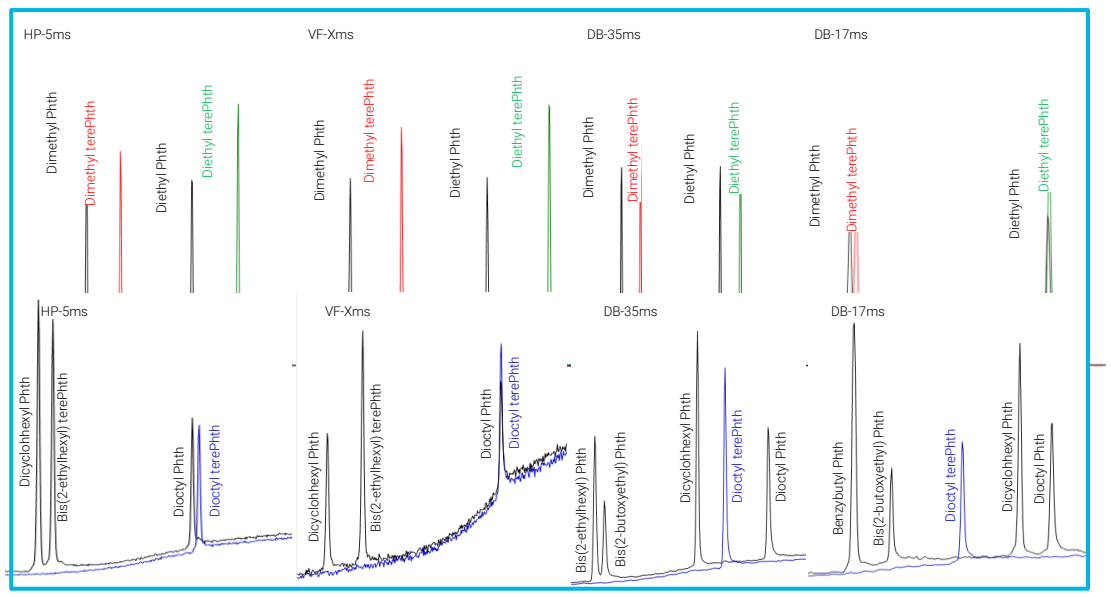

Figure 3. Due to the complexity of the separations, the HP-5ms and DB-35ms were the only columns to baseline separate each of the phthalate isomers. These could not be separated using the MS.

GC Optimization Continued:

The next critical separation is between the phthalates, and nonylphenols, nonylphenol monoethoxylates and nonylphenol diethoxylates. The only major co-elution occurred within the nonylphenol monoethoxylates and a few phthalates. These compounds could be separated using unique ions for each compound at the specified retention time. The HP-5ms and VF-5ms columns showed overlap of the monoethoxylates and both dibutyl and bis(2-methoxyethyl) phthalate. Only Dibutyl phthalate eluted within the monoethoxylates on the DB-35ms and the DB-17ms (Figure 4). The DB-35ms phase was selected as the best phase to separate the analytes; for the optimized method a 20 m x 0.18 mm x 0.18 µm DB-35ms was optimized for minimal runtime (Figure 5).

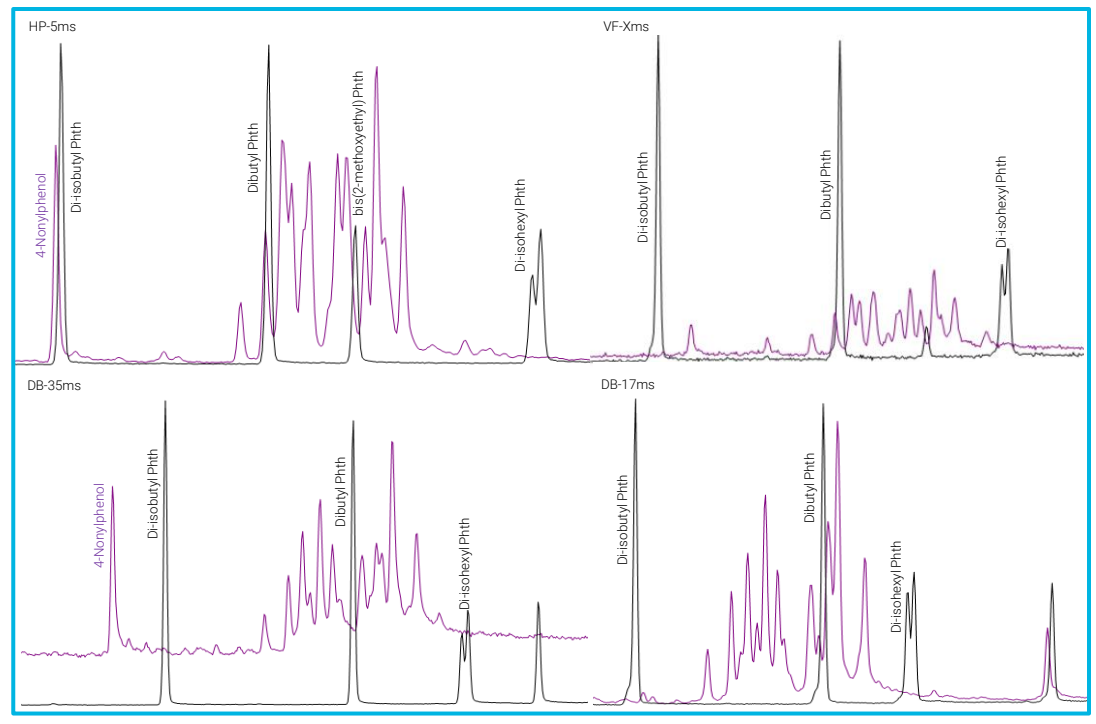

Figure 4. Overlaid chromatogram for the four columns tested to illustrate the need for a higher polarity column to help separate the phthalates and the nonylphenol monoethoxylate isomers. 4-nonylphenol and di-isobutyl phthalate almost co-elute on the HP-5ms column.

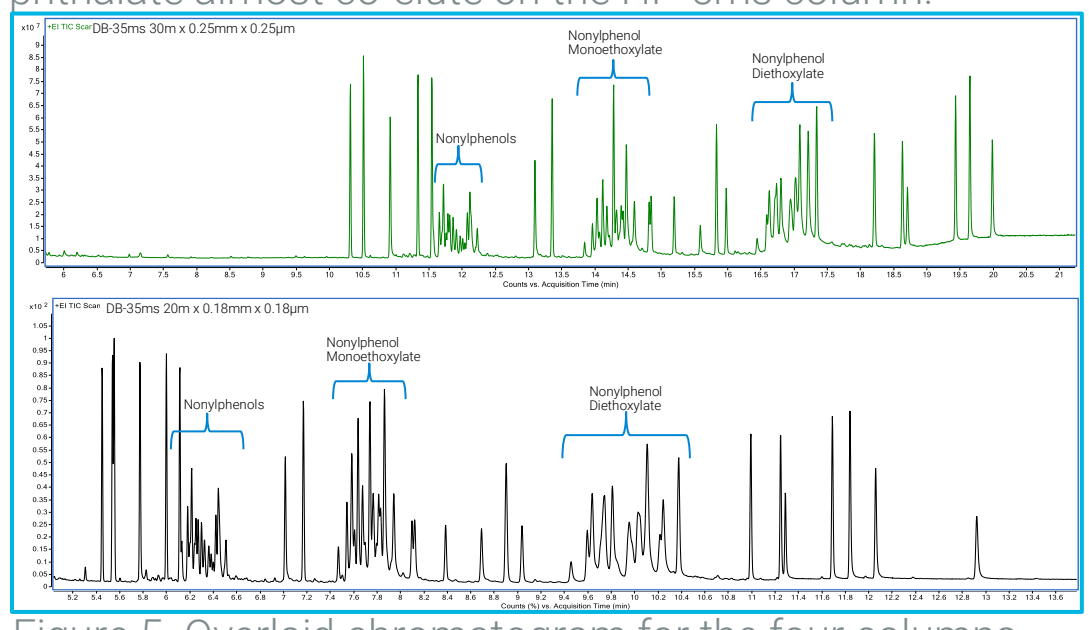

Figure 5. Overlaid chromatogram for the four columns tested to illustrate the need for a higher polarity column to help separate the phthalates and the nonylphenol monoethoxylate isomers. 4-nonylphenol and di-isobutyl phthalate almost co-elute on the HP-5ms column.

Results and Discussion

MS/MS Optimization:

The complexity and number of components in this analysis create a challenge for the method creation. Manually injecting, analyzing the results and creating a method for the next injection will take a significant amount of time for each MRM transition. MRM Optimizer was utilized to automate this process after the GC method was completed. The full scan data from the optimized method is loaded into the software, deconvolution extracts single component spectra which are analyzed and the precursor ions are selected automatically. MRM Optimizer will create the product ion method, run the sample, analyze the results to find the optimal product ions, and finally optimize the collision energy for each transition (Figure 6). Figure 7 provides the chromatograms for the extracted samples.

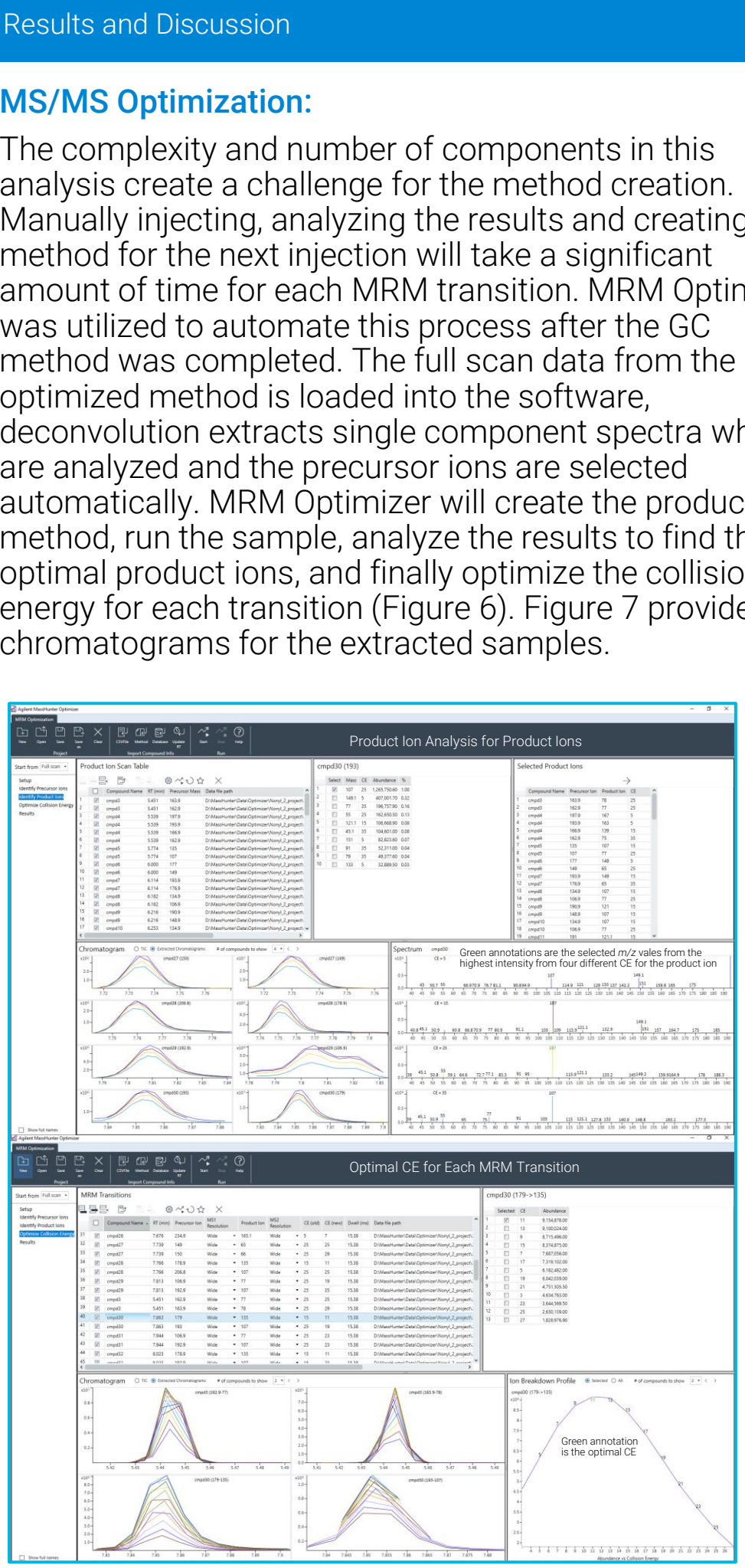

Figure 6. The two main steps for MRM Optimizer to create the MRM transition for the analytes.

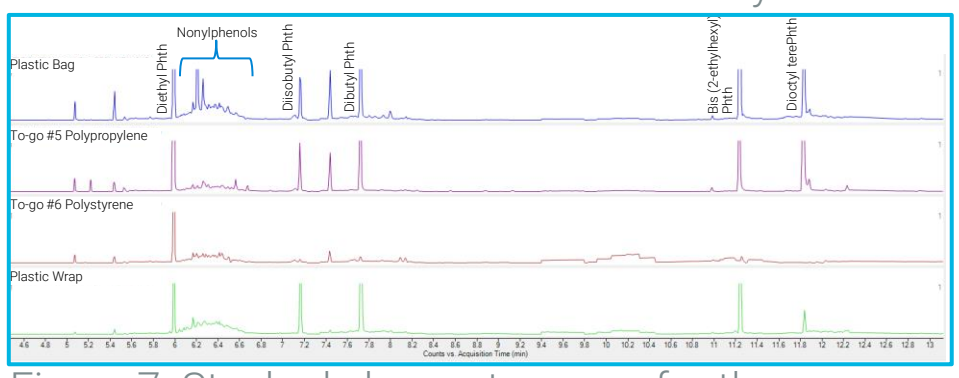

Figure 7. Stacked chromatograms for the extracted plastic packaging material. The wrap and bag both extracted the most nonylphenols.

Phthalates, terephthalates and the nonylphenol standards were all detected at the 1 fg/µL concentration (Figure 8). Diethyl phthalate is not included due to this compound being found in multiple components from the sample prep and introduction. The glassware and glass micro-pipetter were cleaned with multiple solvents prior to the dilutions.

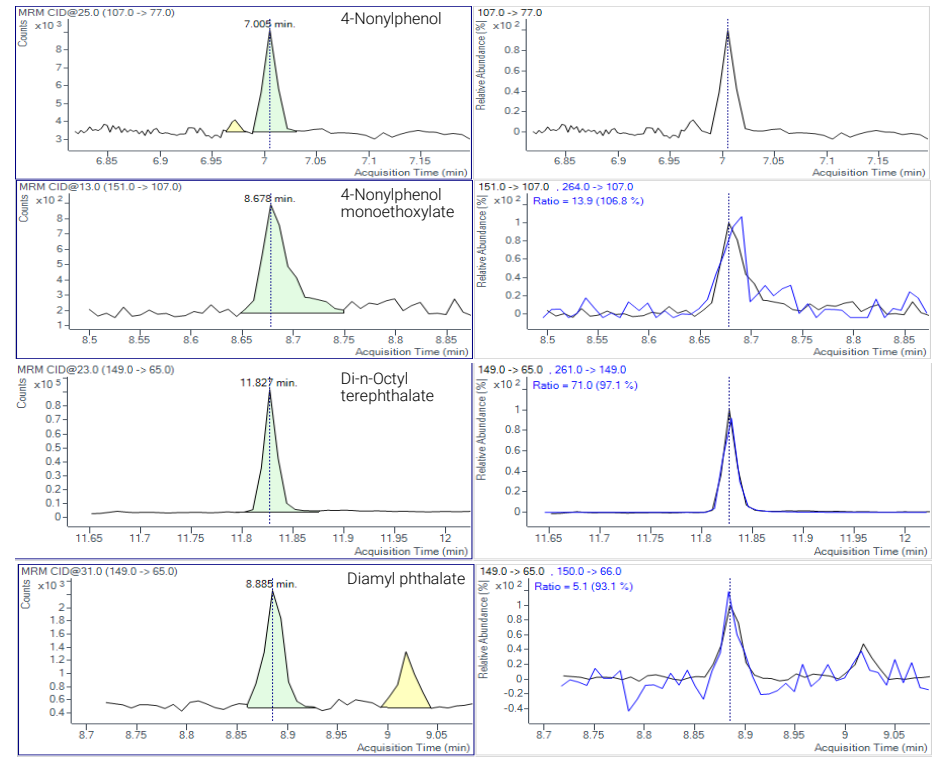

Figure 8. MRM transitions for the phthalate, terephthalate, 4-nonylphenol and 4-nonylphenol monoethoxylate at 1 fg/µL.

Conclusions

- The DB-35ms column and a cold pulsed splitless injection provided the best combination for separation, peak shape and intensity for this analysis.
- The phthalates and terephthalates were detected at the 1 fg μL^{-1} concentration and 4-nonylphenol and 4-nonylphenol monoethoxylate were detected
- Diethyl terephthalate, di-isobutyl phthalate, di-butyl phthalate were all detected in the real-world plastic samples while nonylphenols were only detected in the bag and wrap.
- One of the main difficulties with this analysis is minimizing background from plastic during the sample prep and sample introduction. Dimethyl phthalate was still observed in the blank even with rigorous cleaning.

References

[1]Votavová, L. & Dobiáš, Jaroslav & Voldřich, M. & Čížková, Helena. (2009). Migration of nonylphenols from polymer packaging materials into food simulants. Czech Journal of Food Sciences. 27. 293-299. 10.17221/152/2008-CJFS.

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